National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 189b

Potassium Tetroxalate Dihydrate

pH Standard

Standard Reference Material (SRM) 189b is intended for use in preparing solutions for calibrating electrodes for pH measuring systems. SRM 189b Potassium Tetroxalate Dihydrate [$KH_3(C_2O_4)_2 \cdot 2H_2O$], meets the specifications of the American Chemical Society for reagent grade material [1]. A unit of SRM 189b consists of a bottle containing 65 g of crystalline material. **NOTE:** These certified pH(S) values apply **only** to solutions prepared from this current lot (b) of **SRM 189b**. This SRM is certified for pH(S) **only** and not for acidimetric purposes.

Certified pH Values and Uncertainties: The pH(S) values listed in Table 1 correspond to log ($1/a_H$), where a_H is the conventional activity of the hydrogen (hydronium) ion referred to the standard state (p° = 1 atm = 1.01325 10^5 Pa) on the scale of molality. The values were derived from emf measurements of cells without liquid junction by the method of calculation described in References [2,3]. The expanded uncertainty, $U = ku_c$, at the 95 % confidence level, calculated according to the ISO procedure [4], is less than 0.005 pH units at all temperatures listed. It includes Type B components due to measurements of temperature, pressure, electrode potential, and the gravimetric preparation of standards. The uncertainty also includes Type A components due to the standard deviation of the pH(S) values after smoothing with respect to temperature as described in reference [3], the homogeneity assessment of the SRM material, and the coulometric determination of the molality of HCl used to standardize the electrodes. However, to allow for extra-thermodynamic assumptions in the assignment of pH(S), an expanded uncertainty (k = 2, df $\geq$ 60) of 0.005 pH units is assigned to the pH(S) values at all temperatures from 0 °C to 50 °C. The composition of the material used for this SRM is homogeneous with respect to the certified pH(S) values. However, it contains a slight excess of potassium hydrogen oxalate as compared to the theoretical formula. The certified pH(S) values of SRM 189b are, therefore, greater than the theoretical values for this material.

A solution of SRM 189b with a molality of 0.05 mol/kg with respect to $KH_3(C_2O_4)_2 \cdot 2H_2O$ is recommended for the calibration of pH measuring systems (See Calibrations with SRM 189b in pH Cells with Liquid Junction and Preparation of the 0.05 mol/kg Solution Sections). The pH(S) of a 0.05 mol/kg solution of SRM 189b as a function of temperature, t, is presented in Table 1. No value is certified at t = 0 °C due to solubility restrictions of this material [5].

Table 1. Certified pH(S) Values and Uncertainties for SRM 189b

t/°C	pH(S)	t/°C	pH(S)	t/°C	pH(S)
5.0	1.709 ± 0.005	25.0	1.719 ± 0.005	45.0	1.746 ± 0.005
10.0	1.709 ± 0.005	30.0	1.724 ± 0.005	50.0	1.754 ± 0.005
15.0	1.711 ± 0.005	35.0	1.731 ± 0.005		
20.0	1.714 ± 0.005	40.0	1.738 ± 0.005		

Expiration of Certification: The certification of SRM 189b is valid until **31 December 2005**, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate. However, the certification is invalid if the SRM is damaged, contaminated, or modified.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.C. Colbert.

Willie E. May, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 16 August 2000
SRM 189b

Nancy M. Trahey, Chief
Standard Reference Materials Program

The experimental work leading to the certification of this SRM was performed by K.W. Pratt of the NIST Analytical Chemistry Division.

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

Source of Material: The potassium tetroxalate dihydrate was obtained from a commercial supplier and sieved by NIST to remove coarse particles. [1].

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

INSTRUCTIONS FOR USE

Drying Instructions: Use as received. The crystalline material must **NOT** be dried in an oven or placed in a desiccator before use.

Storage: The unit should be stored, as received, in its original container with the cap tightly closed, under normal laboratory conditions. The SRM should **NOT** be stored in a desiccator.

Calibrations with SRM 189b in pH Cells with Liquid Junction: This SRM is recommended for calibration and for confirmatory purposes in cells with liquid junction. However, the liquid junction potential of the common pH cell displays a greater variability in solutions of pH less than 2.5 than in solutions of pH between 2.5 and 11.5. Hence, the experimental pH in such cells for SRM 189b may differ by 0.02 to 0.05 pH units from the values of pH(S) given in this certificate.

Preparation of the 0.05 mol/kg Solution: Gently crush any large lumps of the crystalline material. Transfer 12.717 g (mass in air) of SRM 189b to a flask and dissolve in 1.000 kg (mass in air) of distilled carbon dioxide-free water. Alternatively, if volumetric apparatus is to be used, transfer 12.584 g (mass in air) to a 1 L volumetric flask, dissolve in distilled or deionized water, and fill to the mark with water at 25 °C. The water should have a conductivity no greater than 2 μS/cm. The solution, being acidic, does not need to be protected with a soda-lime tube. With either method, verify visually that the SRM material has completely dissolved. **NOTE:** The SRM material dissolves slowly. Shaking for 12 h or longer may be necessary to effect complete dissolution.

Stability of Prepared Solution: Solutions prepared from SRM 189b are stable for one month. For the highest accuracy, prepare fresh solutions on a weekly basis.

REFERENCES

[1] Reagent Chemicals, 8th Ed., American Chemical Society, Washington DC, (1993).

[2] Wu, Y.C., Koch, W.F., and Marinenko, G., "A Report on the National Bureau of Standards pH Standards," *J. Res. Natl. Bur. Stand.*, **89**, p. 395, (1984).

[3] Wu, Y.C., Koch, W.F., and Durst, R.A., *Standard Reference Materials: Standardization of pH Measurements*, NBS Spec. Publ. 260-53, (February 1988).

[4] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993); see also Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, U.S. Government Printing Office, Washington DC, (1994); available at http://physics.nist.gov/Pubs/.

[5] Baucke, F.G.K., "Lower Temperature Limit of NBS (DIN) pH Standard Buffer Solution Potassium Tetroxalate," *Electrochimica Acta*, **24**, pp. 95-97, (1979).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.